650. *Olefinic Acids. Part IV. Prototropic and Anionotropic Changes in the α-Bromo-ββ-dimethylacrylic Acid System.*

By L. N. Owen and M. U. S. Sultanbawa.

It is shown that in the reactions of α-bromo-ββ-dimethylacrylic acid (I) with alcoholic alkoxides an initial prototropic change to the βγ-unsaturated isomer (IV) is followed by nucleophilic replacement of the halogen to give the α-alkoxy-β-methylenebutyric acid (III), which by a further prototropic change is converted into the α-alkoxy-ββ-dimethylacrylic acid (II). The interconversion of (II) and (III) has been studied under various conditions. A similar series of changes occurs, though much more rapidly, with the methyl and ethyl esters of (I), and also when the ethyl ester is treated with piperidine, the product then being a mixture of the ethyl α-piperidino-β-methylenebutyrate and α-piperidino-ββ-dimethylacrylate. There is no evidence of any anionotropic change under these conditions. When, however, the bromo-acid reacts with aqueous alkali, the initial prototropic change to the βγ-unsaturated isomer is followed by replacement of the halogen in two ways, (i) by normal replacement, to give *α-hydroxy-β-methylenebutyric acid*, and (ii) with anionotropic rearrangement to give *γ-hydroxy-β-methylcrotonic acid*; the α-hydroxy-β-methylenebutyric acid also undergoes prototropic change to α-keto*iso*-valeric acid. Each of the three products has been identified in the reaction mixture.

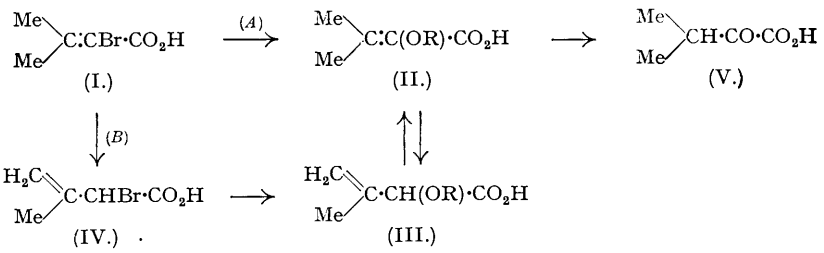
The occurrence of the prototropic change in the original bromo-acid accounts for its reactivity, since the bromine atom is then no longer attached to an ethylenic carbon atom. This explanation is probably of general application, *e.g.*, to α-bromocrotonic acid; with α-bromoacrylic acid, in which such prototropy is not possible, no " substitution " of halogen occurs.

The theoretical interpretation of the various changes is dicussed in terms of the electronic characteristics of the groups involved. The greater reactivity of the bromo-acids, compared with their chloro-analogues, suggests that bromine has the greater capacity for electron withdrawal; this reversal of the normal order of the inductive ($-I$) effects is attributed to the possession, by chlorine, of a relatively much larger $+M$ effect.

In Part III (Owen, this vol., p. 236) it was shown that treatment of α-bromo-ββ-dimethylacrylic acid (I) with alcoholic alkoxides led to the formation of a mixture of the α-alkoxy-ββ-dimethylacrylic acid (II) and the α-alkoxy-β-methylenebutyric acid (III). The formation of the βγ-unsaturated isomer was unexpected, since no rearrangement had been observed under similar conditions in the crotonic acid series (Part I; Owen, *J.*, 1945, 385), but it was pointed out that there were two ways in which the result could be explained. At the time, the available evidence was insufficient for a decision to be made, and the reaction has therefore been investigated in greater detail.

The two possible mechanisms are : (*A*) direct nucleophilic replacement of the bromine atom in (I) to give (II), followed by prototropic isomerisation of (II) to (III); and (*B*) prototropic

change within the bromo-acid (I) to give (IV), followed by nucleophilic replacement, to yield (III), and a further prototropic change to (II). If the first mechanism is correct, the amount of (III)



should increase, relative to (II), as the reaction proceeds (assuming that their interconversion is not very rapid); on the other hand, mechanism (*B*) requires an increase of (II) relative to (III). Two portions of the bromo-acid were therefore heated under identical conditions with excess of methanolic sodium methoxide for 6 and 24 hours respectively, preliminary experiments having shown that the liberation of bromide ion was practically complete in 6 hours. The amount of α-methoxy-ββ-dimethylacrylic acid (II; R = Me) produced was estimated as the 2 : 4-dinitrophenylhydrazone of α-keto*iso*valeric acid (V), and was found to be considerably greater with the longer period of heating. This result was supported by larger-scale experiments in which it was found that the solid isomer (II; R = Me) readily crystallised from the 24-hours reaction product; the shorter reaction period gave only traces of this material, the main product then being the liquid isomer (III; R = Me). These results gave the first definite evidence in favour of mechanism (*B*), which was also supported by the following observations. α-Methoxy-β-methylenebutyric acid (III; R = Me) was heated with aqueous sodium hydroxide of different concentrations for 24 hours at 100°; the amount of conversion into the αβ-form (II; R = Me), estimated as before, was found to increase with the concentration; this provided a useful method for obtaining the solid isomer—by heating the liquid acid (III; R = Me) with 5N-aqueous alkali at 100° for 24 hours. Similar results were obtained with the ethoxy-acids; thus, the liquid βγ-form (III; R = Et) was readily converted into the solid α-ethoxy-ββ-dimethylacrylic acid (II; R = Et).

The prototropic change of (III) to (II) was also readily followed by observations of the changes in ultra-violet-light absorption, since only the conjugated acids (II) exhibit maximum selective absorption within the usual range of measurement. In applying this method, it was found that aqueous solutions could not be used, since the maximum was then displaced to a lower wave-length, but in ethanol the results were satisfactory, provided, for the same reason, that the acids were present in the free state and not as sodium salts; displacement of the maximum evidently occurs also in the ionised form. The method adopted, and used not only for the present problem but for other related investigations described later, was as follows. The acid (αβ- or βγ-unsaturated form) was equilibrated with a known amount of standard ethanolic sodium ethoxide at 100°, then neutralised with alcoholic hydrogen chloride equivalent to the ethoxide, dilute with ethanol, and filtered; the light absorption was then measured for the filtrate. In this way it was found that the equilibrium position, reached from either (II) or (III), lay very largely on the αβ-side, being *ca.* 80% for R = Et, and over 90% for R = Me (see table).

Equilibration with 2·6N-ethanolic sodium ethoxide at 100°.

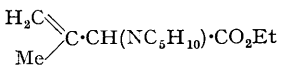
Acid.	Time, hr.	ε at $\lambda_{max.}$ 2280 A.	Acid.	Time, hr.	ε at $\lambda_{max.}$ 2280 A.
(III; R=Me)	0	1,950 *	(III; R=Et)	0	2,900 *
(III; R=Me)	18	8,850	(III; R=Et)	18	10,400
(III; R=Me)	42	9,100	(II; R=Et)	0	12,400
(II; R=Me)	0	10,000	(II; R=Et)	18	10,100
(II; R=Me)	18	9,360			

* The βγ-unsaturated acid contained *ca.* 20% of the αβ-form.

In view of the above results it was of interest to investigate the reactions of the corresponding esters, since they would be expected to exhibit mobilities of the prototropic system greater than those of the acids. This was found to be so. The halogen atom in methyl α-bromo-ββ-dimethylacrylate was completely removed by treatment with 3N-methanolic sodium methoxide at room temperature for 24 hours, to give mainly *methyl α-methoxy-ββ-dimethylacrylate*, the structure of which was confirmed by the high intensity of its light absorption (ε = 11,800 at $\lambda_{max.}$ 2300 A.),

and by hydrolysis to the crystalline acid (II; R = Me). Esterification of α-methoxy-β-methylenebutyric acid (III; R = Me) with diazomethane gave the *methyl* ester, which differed from the αβ-unsaturated isomer in having a lower refractive index and in showing no selective light absorption; it was, however, very largely converted into the latter ester when kept at ordinary temperature in methanolic sodium methoxide. Hydrolysis of methyl α-methoxy-β-methylenebutyrate, which was effected by boiling with aqueous alkali for ½ hour, gave its own acid, thus indicating that the rate of hydrolysis was much greater than that of conversion into the αβ-unsaturated ester. This period of heating was insufficient to convert any appreciable amount of the acid itself into the αβ-isomer, since the mobility of the acid must be considerably less than that of the ester. Similar observations were made with the ethyl esters; thus, treatment of ethyl α-bromo-ββ-dimethylacrylate with cold ethanolic sodium ethoxide gave *ethyl α-ethoxy-ββ-dimethylacrylate*, which was also obtained by action of the same reagent on ethyl α-ethoxy-β-methylenebutyrate. The structure of the αβ-unsaturated ester was confirmed by its light absorption (ε = 8950 at $\lambda_{max.}$ 2300 A.) and by hydrolysis to solid α-ethoxy-ββ-dimethylacrylic acid.

In Part III (*loc. cit.*) it was suggested that the products described by Murfitt and Roberts (*J.*, 1944, 371) as ethyl α-piperidino- and α-bisdimethylamino-ββ-dimethylacrylate were probably the βγ-unsaturated isomers. This view, however, was rendered less certain by the high mobilities encountered in the reactions of the bromo-esters with alkoxides, in which the end products were the αβ-unsaturated alkoxy-esters. Ethyl α-bromo-ββ-dimethylacrylate was therefore treated with piperidine, under the conditions specified by Murfitt and Roberts, and gave a product which showed ε = 2850 at $\lambda_{max.}$ 2190 A. This intensity of light absorption was too low for a pure αβ-unsaturated ester, and the presence of a major proportion of ethyl α-piperidino-β-methylene-butyrate (VI) was proved by ozonolysis, a considerable amount of formaldehyde being evolved. Furthermore, the reaction mixture, on treatment with cold dry ethanolic sodium ethoxide, was very largely converted into *ethyl α-piperidino-ββ-dimethylacrylate* (VII), as shown by the higher refractive index and greater intensity of light absorption (ε = 8860 at $\lambda_{max.}$ 2270 A.); only a trace of formaldehyde was obtained on ozonolysis. Clearly, therefore, the mobility of the βγ-unsaturated piperidino-compound is sufficiently low in the piperidine solution for the compound to persist in large amount in the reaction mixture; with the more active ethoxide catalyst, however, the mobility is raised to such an extent that the αβ-compound (VII) is rapidly formed. An interesting result was obtained when a further portion of the mixed piperidino-ester, consisting largely of (VI), was heated with aqueous alkali; partial hydrolysis took place, and the recovered ester showed an increased intensity of light absorption, thus indicating that the βγ-form had been preferentially hydrolysed; this was confirmed by isolation of the resulting acid, which proved to be α-piperidino-β-methylenebutyric acid, the *sulphate* of which showed no selective light absorption. The ethyl α-piperidino-ββ-dimethylacrylate (VII) was very resistant to hydrolysis. This provides a further example of the greater ease of hydrolysis shown by βγ-unsaturated esters, compared with their αβ-isomers (cf. Eccott and Linstead, *J.*, 1929, 2153).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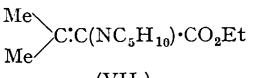
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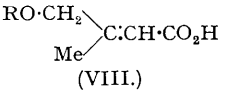

(VIII.)

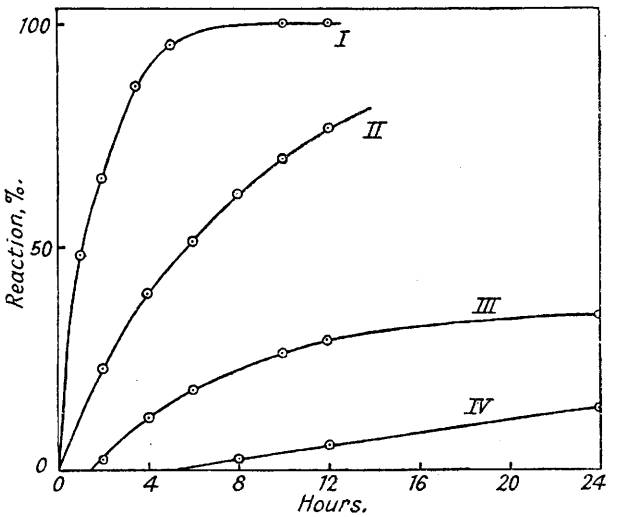
There can therefore be no doubt that the reactions of the esters of α-bromo-ββ-dimethylacrylic acid with alkoxides and with organic bases parallel those of the acid itself, and take place by an initial prototropic change analogous to that involved in mechanism (*B*) discussed above.

An important consequence of the established mechanism is that the rearraged bromo-acid (IV) contains a typical anionotropic grouping, >C:C·CBr. Theoretically, therefore, replacement of the bromine atom might occur, not only directly to give (III), but also with accompanying rearrangement to give the γ-alkoxy-αβ-unsaturated acid (VIII). Such rearrangement is known not to occur under bimolecular conditions, but only when an S_N1 mechanism is possible; *i.e.*, it is facilitated by a solvent of high dielectric constant. Thus, Roberts, Young, and Winstein (*J. Amer. Chem. Soc.*, 1942, **64**, 2157) and Catchpole and Hughes (*J.*, 1948, 4) obtained only the direct substitution products on treatment of α- and γ-methylallyl chloride with dry ethanolic sodium ethoxide; when these chlorides were hydrolysed with aqueous or aqueous-alcoholic alkali, however, the direct and the rearranged product were both formed. It was also shown that the secondary halide reacted only by an S_N1 mechanism, whilst the primary halide involved the participation of S_N1 and S_N2 reactions. Such considerations account for the fact that no

compounds of type (VIII) resulted from the reactions of the bromo-acid (I) with alcoholic alkoxides, but evidently suggest that under aqueous conditions the intermediate (IV) should react at least partly with rearrangement, particularly since it is a secondary bromide.

Preliminary experiments were carried out by heating the bromo-acid (I) with N- and with 2N-aqueous alkali, the replacement of bromine and the formation of α-keto*iso*valeric acid (V) being estimated quantitatively, the latter as the 2 : 4-dinitrophenylhydrazone. The results (see figure) showed that at both concentrations the amount of keto-acid continued to increase after all the bromine had been replaced, thus indicating that it was formed by prototropic change of (IX) to (X), followed by ketonisation of the latter. The intermediate formation of the βγ-unsaturated acid (IX) was proved by the detection of formaldehyde on ozonisation of the product obtained by a 24-hours treatment of the bromo-acid (I) with N-alkali. The observation that the yield of keto-acid, even after prolonged heating, was not more than 50%, suggested that the rearranged product (XI) had also been formed.

The action of aqueous alkali at 100° *on α-bromo-ββ-dimethylacrylic acid.*



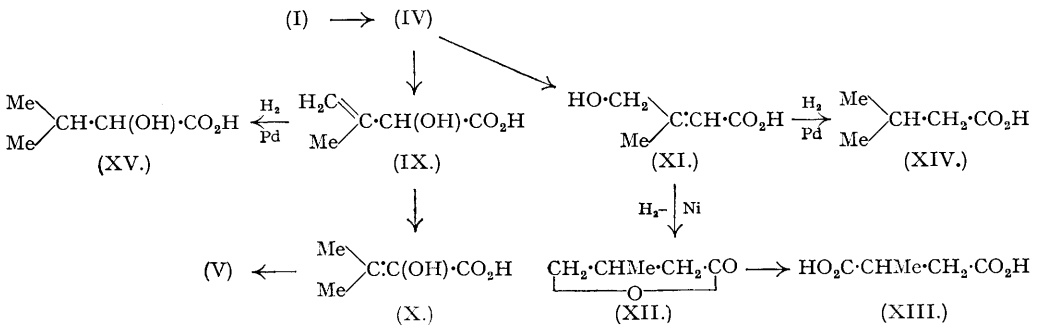
I, *Liberation of bromide ion by* 2N-NaOH. II, *Liberation of bromide ion by* N-NaOH. III, *Formation of keto-acid by* 2N-NaOH. IV, *Formation of keto-acid by* N-NaOH. (*Slight losses of the* 2 : 4-*dinitrophenylhydrazone, owing to its appreciable solubility in water, account for the displacement of curves* III *and* IV *from the origin.*)

The bromo-acid (I) was therefore treated with excess of 2N-sodium hydroxide for 9 hours. The product was a mixture of keto- and unsaturated acids, from which α-keto*iso*valeric acid was removed by distillation as a low-boiling fraction. The higher-boiling material furnished two main products: (i) crystalline *γ-hydroxy-β-methylcrotonic acid* (XI) and (ii) liquid α-hydroxy-β-methylenebutyric acid (IX), which could not be entirely freed from small amounts of (XI). Conclusive proof of the structures of these important products was obtained as follows.

On ozonolysis, (XI) gave acetol (characterised as the 2 : 4-dinitrophenylosazone) but no formaldehyde. In sodium carbonate solution it took up 1 mol. of hydrogen over a Raney nickel catalyst; the resulting γ-hydroxy-β-methylbutyric acid was isolated as the lactone (XII), previously described by Sircar (*J.*, 1928, 899), which on oxidation with chromic acid gave methylsuccinic acid (XIII). An unexpected result was obtained when the hydrogenation of (XI) was carried out in aqueous solution over a palladium–charcoal catalyst: hydrogenolysis occurred and the product was *iso*valeric acid (XIV). It is known (cf. Gilman, "Organic Chemistry," 2nd edn., Vol. I, p. 820) that αβ-unsaturated alcohols undergo hydrogenolysis, but they have not hitherto been found to do so under such mild conditions; the system $OH{\cdot}CH_2{\cdot}CR{:}CH{\cdot}CO_2H$ appears to be particularly susceptible, since we have observed that butyric acid is formed by hydrogenation of γ-hydroxycrotonic acid under the same conditions.

Ozonolysis of the liquid acid (IX) gave formaldehyde and acetol. Owing to the presence in it of a small proportion of (XI), some difficulty was expected in the separation of the products from its hydrogenation, and the following method was devised to overcome this. In a trial experiment it was established that α-hydroxy*iso*valeric acid, the expected product from the

hydrogenation of (IX), was unaffected by hydrogenation in aqueous solution over palladium–charcoal. As mentioned above, however, (XI) was known to undergo hydrogenolysis to



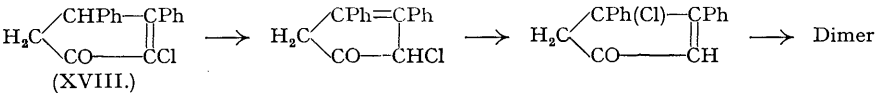
*iso*valeric acid under these conditions. The liquid acid was therefore hydrogenated over this catalyst and gave a mixture of α-hydroxy*iso*valeric (XV) and *iso*valeric acid; the latter distilled with the water on evaporation of the solution, and a solid residue of the hydroxy-acid was obtained, thus confirming the structure of (IX).

When warmed with aqueous alkali, α-hydroxy-β-methylenebutyric acid (IX) gave α-keto*iso*valeric acid, thus establishing the occurrence of the prototropic change (IX) ⟶ (X).

Reactions involving consecutive prototropic and anionotropic changes, such as occur in the treatment of α-bromo-ββ-dimethylacrylic acid with alkali, are very rare. Ingold and Rothstein (*J.*, 1928, 8) obtained the trialkyl-α-ethoxyallylammonium salt (XVII) by the action of sodium ethoxide on the chloro-compound (XVI), and formulated the reaction as follows :

$$\underset{\text{(XVI.)}}{CHCl{:}CH{\cdot}CH_2{\cdot}NR_3X} \longrightarrow CH_2Cl{\cdot}CH{:}CH{\cdot}NR_3X \longrightarrow \underset{\text{(XVII.)}}{CH_2{:}CH{\cdot}CH(OEt){\cdot}NR_3X}$$

A similar series of changes was assumed by Burton and Shoppee (*J.*, 1934, 201) to explain the formation of a dimer from 2-chloro-3 : 4-diphenyl*cyclo*pent-2-enone (XVIII) by the action of alkali :



The work described in the present series of papers was initiated by the observation that the halogen in α-bromocrotonic acid was readily removed as bromide ion by treatment with alkali, in contrast to the reported stability of α-chlorocrotonic acid (cf. Part I, *loc. cit.*). Preliminary experiments have now indicated that, although the chloro-acids are undoubtedly less reactive than their bromo-analogues, the chlorine atom can be removed with alkali of sufficiently high concentration.

Discussion.

The halogen atom in many compounds of the type ·C:CX· is known to be very resistant towards nucleophilic substitution (cf. Hughes, *Trans. Faraday Soc.*, 1938, 194; 1941, 627). In aromatic systems, for example, nuclear halogen compounds, unless activated by the presence of electrophilic groups in the *o*- or *p*-position, are unreactive under ordinary conditions. Compounds such as α-bromo-cinnamic and -maleic acid, on heating with aqueous or alcoholic alkali, give only phenylpropiolic and acetylenedicarboxylic acid, respectively, by elimination of hydrogen bromide, no substitution of halogen being observed :

$$Ph{\cdot}CH{:}CBr{\cdot}CO_2H \longrightarrow Ph{\cdot}C{:}C{\cdot}CO_2H, \text{ and } HO_2C{\cdot}CH{:}CBr{\cdot}CO_2H \longrightarrow HO_2C{\cdot}C{:}C{\cdot}CO_2H$$

The characteristic feature of these compounds is that there is no possibility of a shift of the double bond by prototropic change, such as occurs in the first stage of the reaction of α-bromo-ββ-dimethylacrylic acid with aqueous or alcoholic alkali. The reactivity of the latter acid towards nucleophilic substitution is clearly due to the initial prototropic change, as a result of which the halogen atom is no longer attached to an ethylenic carbon atom. It is therefore very probable that the reactivity of α-bromocrotonic acid towards alkoxides (Part I, *loc. cit.*), in so far as the formation of substitution products is concerned, is due to the operation of a similar mechanism :

$$Me{\cdot}CH{:}CBr{\cdot}CO_2H \longrightarrow CH_2{:}CH{\cdot}CHBr{\cdot}CO_2H \longrightarrow CH_2{:}CH{\cdot}CH(OR){\cdot}CO_2H \longrightarrow Me{\cdot}CH{:}C(OR){\cdot}CO_2H$$

The fact that no α-alkoxy-βγ-unsaturated acid was encountered in this series can be explained by a high rate of conversion into the α-alkoxycrotonic acid; vinylacetic acid is known to isomerise very readily and completely into crotonic acid under alkaline conditions (Linstead and Noble, *J.*, 1934, 614), and the presence of the alkoxy-group in the α-position would be expected to result in an even greater mobility, owing to its $-I$ effect. It is very significant that in the reaction of α-bromoacrylic acid with alkoxides (Part II, *J.*, 1947, 1030) no α-alkoxyacrylic acid could be detected; no αβ ⟶ βγ isomerisation is possible in this case.

In this connection, reference must be made to the claim of Backer and Oosten (*Rec. Trav. chim.*, 1940, **59**, 41) to have prepared tripotassium α-arsonoacrylate by the action of aqueous potassium arsenite on α-bromoacrylic acid:

$$CH_2{:}CBr{\cdot}CO_2H \longrightarrow CH_2{:}C(AsO_3K_2){\cdot}CO_2K$$

Backer and Beute (*ibid.*, 1935, **54**, 200) had originally stated that by a similar reaction, using potassium hydrogen sulphite, they had obtained α-sulphoacrylic acid, but subsequently (*ibid.*, p. 523) they showed that the product was actually β-sulphoacrylic acid, formed by addition of the sulphite and elimination of hydrogen bromide. There appears to be no reason why the arsono-acid, also, should not be formulated as a β-derivative; none of the published evidence precludes such a structure.

Consideration must now be given to a theoretical explanation of the initial prototropic change which occurs in α-bromo-ββ-dimethylacrylic acid. ββ-Dimethylacrylic acid itself cannot be isomerised to β-methylenebutyric acid (Kon and Linstead, *J.*, 1925, **127**, 616), and the only previously recorded isomerisation of a derivative of the former acid is that of ethyl α-nitro-ββ-dimethylacrylate (XIX), which on treatment with alkali gives the βγ-unsaturated isomer (XX) (Bouveault and Wahl, *Bull. Soc. chim.*, 1901, **25**, 801, 814, 918). This transformation is clearly brought about by the powerful electrophilic ($-I$) effect of the nitro-group, which in the first place increases the mobility of the system by facilitating ionisation of the proton, and then, by

(XIX.) $Me_2C{:}C(NO_2){\cdot}CO_2Et$ $\qquad$ $H_2C{=}CMe{\cdot}CH(NO_2){\cdot}CO_2Et$ (XX.)

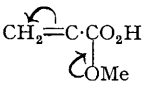
favouring recombination of the proton in the α-position, results in the formation of the βγ-isomer (cf. Baker, "Tautomerism," Routledge, 1934, p. 40). It is evident from the present experimental results that a bromine atom in the α-position must exert an effect similar to that of the nitro-group, with the possible exception that it does not necessarily throw the αβ-βγ equilibrium so completely to the βγ-side, since the βγ-form undergoes further reaction by nucleophilic substitution, thus disturbing any equilibrium which may otherwise have been attained. The electronic properties of the halogens are known to be ($-I$, $+T$), and the variable contribution of the mesomeric ($+M$) portion of the $+T$ effect has been cited in order to explain certain anomalies in their behaviour (see, *inter al.*, Bird and Ingold, *J.*, 1938, 918; De la Mare and Robertson, *J.*, 1948, 100). In the case at present under discussion, an increased mobility and a greater tendency to pass, at least in part, into the βγ-unsaturated form (compared with ββ-dimethylacrylic acid itself) indicate that the $-I$ effect is considerable and overshadows any $+M$ effect. De la Mare, Hughes, and Ingold (*J.*, 1948, 21) have referred to the hyperconjugation energy associated with the system $C{=}\overset{\curvearrowright}{C}{-}\overset{\curvearrowright}{C}{-}Br$; this provides a complementary explanation of the αβ ⟶ βγ isomerisation in the bromo-acid, since the βγ-form would be stabilised by the contribution from such a structure, which acts in opposition to the normal stabilisation of the αβ-form by the hyperconjugation of the methyl groups. In α-bromocrotonic acid the latter hyperconjugation would be less, since only one methyl group is present, and there would consequently be an even greater tendency for the acid to pass into the βγ-form; this accounts for the higher reactivity, towards nucleophilic replacement, of α-bromocrotonic compared with α-bromo-ββ-dimethylacrylic acid (cf. figure, Part I, *loc. cit.*, and figure, this paper).

The much higher reactivity of αβ-unsaturated α-bromo-acids, compared with the chloro-analogues, is presumably caused by the greater readiness with which the former can undergo prototropic change. There has been considerable controversy over the relative electronic effects of the halogens (summarised by De la Mare and Robertson, *loc. cit.*), but in the present case it appears that bromine must have a greater capacity for electron withdrawal than chlorine. This is the reverse of the order of the inductive ($-I$) effects, which is recognised to be F > Cl > Br > I, and suggests that the mesomeric ($+M$) effect of chlorine is relatively more important than that of bromine. This conclusion itself, however, is contrary to the theoretical order of $+T$ effect, *viz.*, F < Cl < Br < I, but agrees with the order of mesomeric effects

suggested by Bennett (*J.*, 1933, 1112) and with the recent observations of Braude and Stern (*J.*, 1947, 1096; see also De la Mare and Robertson, *loc. cit.*). Further comparisons of the reactivities of unsaturated chloro- and bromo-acids may provide more conclusive evidence on this point.

Substitution by an alkoxy-group in the α-position clearly has an effect opposite to that of the nitro-group, in that the equilibrium (II) $\rightleftharpoons$ (III) lies almost entirely on the αβ-side. The $-I$ effect of the alkoxy-group would be expected to increase the mobility of the system, though not to the extent brought about by the much stronger $-I$ effect of the nitro-group; on the other hand, the equilibrium position indicates control by the powerful $+M$ effect. Further evidence in support of this is presented in Part V (following paper).

With regard to the influence of substituents on the additive reactivity of the double bond in the αβ-unsaturated acids, it has been established that in the bromo-acid series, the order of reactivity is $CH_2{:}CBr{\cdot}CO_2H > CHMe{:}CBr{\cdot}CO_2H > CMe_2{:}CBr{\cdot}CO_2H$; substitution by the methyl groups in the β-position increases the electronic charge on the β-carbon atom and consequently hinders the nucleophilic addition of alkoxide ions, which occurs only partly with α-bromocrotonic acid and not at all with α-bromo-ββ-dimethylacrylic acid.† The presence of an alkoxy-group in the α-position, instead of bromine, has a powerful deactivating effect, since even α-methoxyacrylic acid does not undergo addition with alcoholic alkoxides. This must again be attributed to the $+M$ property:



Experimental.

(Light petroleum, unless otherwise stated, was the fraction of b. p. 40—60°. Light absorption, when a solvent is not specified, was determined in ethanol.)

α-Bromo-ββ-dimethylacrylic Acid.—The following procedure was advantageous (cf. Staudinger and Ott, *Ber.*, 1911, **44**, 1599). αβ-Dibromo*iso*valeric acid (120 g.) was dissolved in ethanol (150 c.c.), cooled to 5°, and treated with sodium ethoxide (sodium, 21·35 g.; ethanol, 200 c.c.), added during ½ hour, the temperature being kept below 10° by cooling. After a further 2 hours at 10—15°, a slight excess of 50% sulphuric acid was added (Congo-red); the precipitated sodium sulphate was filtered off and the filtrate evaporated under reduced pressure. The residue crystallised on stirring it with cold water. The bromo-acid was recrystallised from light petroleum. Yield 64 g. (77·5%); m. p. 91·5°.

Reaction of α-Bromo-ββ-dimethylacrylic Acid with Sodium Methoxide.—(*a*) The acid (0·45 g.) in methanol (1 c.c.) was mixed with 4·3N-methanolic sodium methoxide (4 c.c.), boiled under reflux for 6 hours, cooled, and treated with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate. After 14 days, the 2 : 4-dinitrophenylhydrazone of α-keto*iso*valeric acid was collected and dried (0·26 g., 35%).

(*b*) As above, but with 24 hours' heating. Yield, 0·48 g. (65%).

(*c*) To a solution of bromo-acid (18 g.) in methanol (50 c.c.), 4·3N-methanolic sodium methoxide (120 c.c.) was added; the mixture was heated under reflux for 8 hours and then evaporated under reduced pressure. The residue was dissolved in water, acidified (Congo-red) with 4N-sulphuric acid, and immediately extracted with ether. Evaporation of the dried (Na_2SO_4) extracts gave an oil which on distillation furnished 10·65 g. (81·5%), b. p. 82—84°/1 mm., from which a trace of solid α-methoxy-ββ-dimethylacrylic acid crystallised on storage. Fractional distillation of the liquid acid gave a series of fractions with light absorption of $\lambda_{max.}$ 2240A.; ε 1560—3510; they thus contained from 15—35% of the αβ-unsaturated acid.

(*d*) The bromo-acid (1·8 g.), methanol (5 c.c.), and 5N-sodium methoxide (10 c.c.) were heated under reflux for 24 hours and then worked up as in the previous experiment. The oil (0·94 g.) partly crystallised and gave 0·32 g. of solid α-methoxy-ββ-dimethylacrylic acid.

Conversion of α-Methoxymethylenebutyric into α-Methoxy-ββ-dimethylacrylic Acid.—(*a*) The liquid βγ-unsaturated acid (0·42 g.) was heated at 100° with aqueous sodium hydroxide solution, of various concentrations, for 24 hours, and then acidified and treated with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate:

Alkali concentration :	0.	N.	2N.	10N.
Yield of derivative, %	10 *	27	55	73

* Blank determination (the acid contained a small proportion of the αβ-unsaturated isomer).

(*b*) The βγ-unsaturated acid (1·0 g.) was heated with aqueous 5N-sodium hydroxide (10 c.c.) for 24 hours at 100°. The cooled solution was acidified (Congo-red) with 2N-hydrochloric acid and immediately extracted with ether. Evaporation of the dried ($CaCl_2$) extract gave a solid residue of α-methoxy-ββ-dimethylacrylic acid (0·8 g.), m. p. 70·5° after crystallisation from light petroleum (b. p. 60—80°).

Reaction of α-Bromo-ββ-dimethylacrylic Acid with Sodium Ethoxide (cf. Owen, Part III, *loc. cit.*).—The bromo-acid (18 g.) was heated under reflux with 2·7N-ethanolic sodium ethoxide (120 c.c.) for 14 hours. The solution was evaporated, and the residue was acidified with 2N-hydrochloric acid (Congo-red) and extracted with ether to yield an oil, distillation of which gave (i) 8·3 g., b. p. 90—100°/3 mm., and (ii) 3·75 g., b. p. 100°/3 mm. The second fraction solidified, and on recrystallisation from light petroleum gave α-ethoxy-ββ-dimethylacrylic acid, m. p. 55°, which formed a *p-phenylphenacyl* ester, needles, m. p. 106°, from alcohol (Found: C, 74·1; H, 6·3. $C_{21}H_{22}O_4$ requires C, 74·5; H, 6·55%). On storage, the first fraction deposited a small amount (1·2 g.) of the same solid acid, but consisted mainly of α-ethoxy-β-

† The observation (Part I, *loc. cit.*) that with α-bromocrotonic acid the proportion of β-alkoxy-derivative (formed by addition of alkoxide and subsequent loss of hydrogen bromide) increases in the order Me < Et < Pr^i < Bu^t, is in accord with the increasing nucleophilic properties of these groups.

methylenebutyric acid, the p-*phenylphenacyl* ester of which crystallised from alcohol in leaflets, m. p. 62—63·5° (Found: C, 74·1; H, 6·5. $C_{21}H_{22}O_4$ requires C, 74·5; H, 6·55%).

Conversion of α-Ethoxy-β-methylenebutyric into α-Ethoxy-ββ-dimethylacrylic Acid.—The βγ-unsaturated acid (0·82 g.) was heated with aqueous 5N-sodium hydroxide (10 c.c.) for 24 hours at 100°. The product was isolated as for the methoxy-analogue and formed a solid residue (0·7 g.) which crystallised from water in needles, m. p. 55°.

Equilibration of α-Methoxy-β-methylenebutyric and α-Methoxy-ββ-dimethylacrylic Acid.—Portions of the acid (*ca.* 10 mg.) were heated with 2·6N-ethanolic sodium ethoxide (1 c.c.) in a sealed tube at 95—98°, for various times. The cooled solutions were transferred to 50-c.c. flasks and neutralised by the addition of the pre-determined amount of 0·1N-ethanolic hydrogen chloride (*i.e.*, equivalent to 1 c.c. of sodium ethoxide). After dilution with ethanol to 50 c.c., the solutions were filtered, and the light absorption immediately determined. The results have been given in the table.

Methyl α-Bromo-ββ-dimethylacrylate.—α-Bromo-ββ-dimethylacrylic acid (20 g.) was dissolved in ether, cooled to 0°, and treated with an ethereal solution of diazomethane until a slight yellow colour persisted for a few minutes. Evaporation, and distillation of the residue, gave the methyl ester (18·6 g.), b. p. 88—90°/25 mm., n_D^{22} 1·4926.

Reaction of Methyl α-Bromo-ββ-dimethylacrylate with Sodium Methoxide.—A solution of the bromo-ester (9·6 g.) in methanol (10 c.c.) was added to methanolic sodium methoxide (sodium, 5 g.; methanol, 75 c.c.). After 24 hours at *ca.* 20° the solution was neutralised with aqueous hydrochloric acid and extracted with ether. Evaporation of the dried ($CaCl_2$) extracts gave an oil which on fractionation yielded *methyl α-methoxy-ββ-dimethylacrylate* (5·15 g., 72%), b. p. 78—79°/25 mm., n_D^{21} 1·4451 (Found: C, 58·6; H, 8·3. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%). Light absorption: $\lambda_{max.}$ 2300 A.; ε = 11,810. A portion of the ester (1·9 g.) was dissolved in methanol (15 c.c.), mixed with aqueous 5N-sodium hydroxide (12·5 c.c.), heated under reflux for ½ hour, diluted with water, and extracted with ether (to remove a trace of oil). The aqueous solution was then acidified (Congo-red) with N-sulphuric acid and extracted with ether. Removal of solvent from the dried ($CaCl_2$) extracts gave a solid residue of α-methoxy-ββ-dimethylacrylic acid, m. p. 70·5°, after crystallisation from light petroleum. The p-*phenylphenacyl* ester formed needles (from alcohol), m. p. 89° (Found: C, 73·9; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

Methyl α-Methoxy-β-methylenebutyrate.—α-Methoxy-β-methylenebutyric acid (5·3 g.), esterified by treatment with the calculated amount of ethereal diazomethane, gave the *methyl* ester (4·95 g.) b. p. 71—72°/21 mm., n_D^{22} 1·4310 (Found: C, 58·6; H, 8·7. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%). Light absorption: no maximum above 2200 A. When the ester (0·7 g.), methanol (5 c.c.), and aqueous 5N-sodium hydroxide (5 c.c.) were set aside at 20° for ½ hour and then heated under reflux for ½ hour, the acid, isolated in the usual way, did not yield any solid αβ-unsaturated isomer and was mainly α-methoxy-β-methylenebutyric acid. The ester is therefore hydrolysed much more rapidly than it is isomerised.

Action of Sodium Methoxide on Methyl α-Methoxy-β-methylenebutyric Acid.—A solution of the ester (4 g.) in methanolic sodium methoxide (sodium, 2·5 g.; methanol, 35 c.c.) was kept for 24 hours at *ca.* 20°, then diluted with water, and extracted with ether. The recovered ester (2·4 g.), b. p. 84—86°/39 mm., n_D^{20} 1·4433, contained *ca.* 77% of methyl α-methoxy-ββ-dimethylacrylate. Light absorption: $\lambda_{max.}$ 2320 A.; ε = 9080. This was confirmed by hydrolysis of a portion (0·8 g.) by heating it under reflux in methanol (7 c.c.) with aqueous 5N-sodium hydroxide (5 c.c.) for ½ hour, the solid α-methoxy-ββ-dimethylacrylic acid, m. p. 70°, being readily isolated.

Reaction of Ethyl α-Bromo-ββ-dimethylacrylate with Sodium Ethoxide.—A solution of the bromo-ester (10·1 g.) in ethanol (5 c.c.) was added to ethanolic sodium ethoxide (sodium, 5 g.; ethanol, 75 c.c.). The mixture became turbid and warm; it was cooled to 20° and set aside at room temperature for 24 hours. The excess of alkali was neutralised with 4N-sulphuric acid, and after dilution with water the solution was extracted with ether, to yield *ethyl α-ethoxy-ββ-dimethylacrylate* (4·8 g., 56%), b. p. 96°/34 mm., n_D^{23} 1·4393 (Found: C, 62·4; H, 9·0. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%). Light absorption: $\lambda_{max.}$ 2300 A.; ε = 8950. A portion of the ester (0·8 g.) was hydrolysed by heating it under reflux for ½ hour with ethanol (5 c.c.) and aqueous 5N-sodium hydroxide (5 c.c.). After being worked up in the same way as for the corresponding methoxy-compound (see above) α-ethoxy-ββ-dimethylacrylic acid (0·54 g.), m. p. 55—56°, was obtained.

Ethyl α-Ethoxy-β-methylenebutyrate.—α-Ethoxy-β-methylenebutyric acid (5·1 g., containing a small proportion of αβ-unsaturated isomer) was dissolved in ethyl iodide (15 c.c.) and treated with silver oxide (7 g.) in small portions. A vigorous reaction occurred. After a further hour, dry ether was added, and the filtered solution was evaporated to an oil, distillation of which gave the *ethyl* ester (4·7 g.), b. p. 82—83°/15 mm., n_D^{20} 1·4310 (Found: C, 62·5; H, 9·45. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%). The presence of some of the αβ-unsaturated ester was indicated by the light absorption, $\lambda_{max.}$ 2280 A.; ε = 4820. Separation by distillation could not be effected and the mixture was therefore used for the following experiment.

Action of Sodium Ethoxide on Ethyl α-Ethoxy-β-methylenebutyrate.—The above ester (4·0 g.) in ethanol (10 c.c.) was mixed with ethanolic sodium ethoxide (sodium, 3 g.; ethanol, 40 c.c.). After 24 hours at *ca.* 20° the product was isolated as for the analogous methoxy-compound, and gave 1·6 g., b. p. 98°/31 mm., n_D^{19} 1·4392. Light absorption: $\lambda_{max.}$ 2280 A.; ε = 9290; $\lambda_{infl.}$ 2340 A.; ε = 8600. The product was therefore mainly αβ-unsaturated ester; this was confirmed by hydrolysis of a portion (0·7 g.) by heating it under reflux with ethanol (5 c.c.) and aqueous 5N-sodium hydroxide (5 c.c.) for ½ hour, whereupon solid α-ethoxy-ββ-dimethylacrylic acid (0·44 g.), m. p. and mixed m. p. 55°, was obtained.

Reaction of Ethyl α-Bromo-ββ-dimethylacrylate with Piperidine.—The ester (20 g.) was dissolved in 95% ethanol (32 c.c.) and piperidine (28 c.c.), set aside at *ca.* 20° for 5 days, and worked up by the procedure of Murfitt and Roberts (*loc. cit.*). The product (12·9 g.), b. p. 78—80°/1 mm., n_D^{22} 1·4668, was a mixture of ethyl α-piperidino-β-methylenebutyrate and ethyl α-piperidino-ββ-dimethylacrylate. Light absorption: $\lambda_{max.}$ 2190 A.; ε = 2850. Ozonolysis of a portion in carbon tetrachloride solution gave formaldehyde, identified in the wash-water by formation of a copious precipitate of the dimedon derivative, m. p. 188°.

Hydrolysis of the Piperidino-ester.—A portion (1 g.) was dissolved in methanol (10 c.c.) and heated with 5N-sodium hydroxide (5 c.c.) for 45 minutes on the steam-bath; hydrolysis was not complete (oily globules still present). Water was added and the unchanged ester was extracted with ether; the recovered material (0·30 g.), b. p. 82°/1 mm., n_D^{21} 1·4768, contained a higher proportion of the $\alpha\beta$-unsaturated form. Light absorption: $\lambda_{max.}$ 2280 A.; $\varepsilon = 5490$. The alkaline solution was acidified with a slight excess of sulphuric acid (Congo-red) and evaporated to dryness. Extraction of the residue with methanol gave an oil which partly crystallised. The solid was drained on porous tile and gave the *sulphate* of α-piperidino-β-methylenebutyric acid, which formed leaflets, m. p. 210—212°, from methanol–ether (Found: C, 51·9; H, 7·7; N, 5·9. $C_{10}H_{17}O_2N,\frac{1}{2}H_2SO_4$ requires C, 51·7; H, 7·8; N, 6·0%).

Action of Sodium Ethoxide on the Piperidino-ester.—A solution of the ester (4·4 g.) in ethanol (10 c.c.) was added to ethanolic sodium ethoxide (sodium, 3 g.; ethanol, 40 c.c.) and set aside at *ca.* 20° for 24 hours, then diluted with water and extracted with ether to give *ethyl α-piperidino-ββ-dimethylacrylate* (2·9 g.), b. p. 69°/0·4 mm., n_D^{22} 1·4764 (Found: C, 68·2; H, 9·9; N, 6·8. $C_{12}H_{21}O_2N$ requires C, 68·3; H, 10·0; N, 6·6%). Light absorption: $\lambda_{max.}$ 2270 A.; $\varepsilon = 8860$. On ozonolysis of a portion, in carbon tetrachloride, only a trace of formaldehyde was formed. The stability towards hydrolysis was shown by heating a portion (0·58 g.) with 2·5N-methanolic potassium hydroxide (10 c.c.) for 1 hour under reflux. On ether extraction, 0·35 g., b. p. 74°/1 mm., n_D^{20} 1·4771, was recovered.

Reaction of α-Bromo-ββ-dimethylacrylic Acid with Aqueous Alkali.—(*a*) Two equal amounts of the bromo-acid (1·80 g. each) were dissolved, one in N-, and the other in 2N-aqueous sodium hydroxide (50 c.c. each) and heated at 100°. At intervals, 5-c.c. portions were titrated against 0·1N-hydrochloric acid (phenolphthalein), and the alkali consumed, allowing for the neutralisation of 1 mol. by the carboxyl group, was taken to indicate the amount of bromide ion liberated. Each portion, after titration, was treated with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate, and after a few hours the precipitated 2 : 4-dinitrophenylhydrazone of α-keto*iso*valeric acid was collected, dried, and weighed. The results are shown in the figure.

(*b*) The bromo-acid (0·9 g.) was heated with N-aqueous sodium hydroxide (25 c.c.) for 24 hours at 100°. The solution was acidified and extracted with ether. Evaporation of the extracts gave an oil (0·44 g.), which was dissolved in acetic acid (10 c.c.) and treated with a stream of ozonised oxygen for ½ hour; after addition of water and zinc dust the product was steam-distilled, and the presence of formaldehyde in the distillate confirmed by formation of the dimedon derivative, m. p. 188°.

(*c*) The bromo-acid (18 g.) was dissolved in aqueous 2N-sodium hydroxide (300 c.c.) and heated on the steam-bath for 9 hours. The solution was then cooled, acidified with hydrochloric acid, and extracted with ether (1 × 100 c.c.; 4 × 50 c.c.). Evaporation of the dried ($CaCl_2$) extracts gave an oil (5·25 g.), which after being kept at 0° overnight deposited *γ-hydroxy-β-methylcrotonic acid*; this crystallised from ethyl acetate–light petroleum is prisms (0·6 g.), m. p. 113° (Found: C, 51·5; H, 7·1. $C_5H_8O_3$ requires C, 51·6; H, 6·9%). Light absorption: $\lambda_{infl.}$ 2270 A.; $\varepsilon = 8120$; $\varepsilon = 13{,}460$ at 2190 A. The p-*phenylphenacyl* ester formed needles, m. p. 129°, from alcohol (Found: C, 73·9; H, 6·2. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·85%).

The liquid portion on fractional distillation gave: (i) α-keto*iso*valeric acid (1 g.), b. p. 67—73°/18 mm., n_D^{21} 1·4268, characterised as the 2 : 4-dinitrophenylhydrazone, m. p. 194°; and (ii) mainly *α-hydroxy-β-methylenebutyric acid* (0·9 g.), b. p. 100° (bath temp.)/0·0001 mm., n_D^{21} 1·4667 (Found: C, 50·5; H, 6·9. $C_5H_8O_3$ requires C, 51·6; H, 6·9%). The latter could not be entirely freed from γ-hydroxy-β-methylcrotonic acid, small amounts of which gradually separated out on long storage.

The aqueous reaction mixture, remaining after the 5 ether extractions, was continuously extracted with ether for 11 hours, and gave an oil (2 g.) from which a further quantity of γ-hydroxy-β-methylcrotonic acid (0·9 g.) crystallised. The total yield of this acid was 1·9 g. (16%).

Proof of Structure of γ-Hydroxy-β-methylcrotonic Acid.—Ozonisation. The acid (0·4 g.) in acetic acid (10 c.c.) was ozonised for 1 hour, the issuing gases being passed through water; no formaldehyde could be detected in this wash-water. The solution was then treated with water and zinc dust, and steam-distilled; no formaldehyde was present in the distillate, though a small amount of acetol was detected as the 2 : 4-dinitrophenylosazone. A further quantity of this derivative was obtained by distillation of the filtered residual aqueous acetic acid solution, and treatment of the distillate with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate on the steam-bath for 2 hours. It formed red needles, m. p. 306°, from nitrobenzene (Found: N, 25·5. Calc. for $C_{15}H_{12}O_8N_8$: N, 25·9%). Some unchanged γ-hydroxy-β-methylcrotonic acid was recovered from the dry residue after distillation of the aqueous acetic acid solution.

Hydrogenation. (*a*) A solution of the acid (1·1 g.) and sodium carbonate (0·8 g.) in water (20 c.c.) was shaken with hydrogen in the presence of Raney nickel (*ca.* 0·2 g.). After 3 hours, 90% of the theoretical amount of hydrogen had been absorbed; this was increased to 98% after a further 13·5 hours, with two fresh additions of catalyst. The filtered solution was then concentrated to *ca.* 15 c.c., acidified with 10N-hydrochloric acid (3 c.c.), and heated on the steam-bath for 1½ hours to effect lactonisation. It was cooled, treated with excess of sodium hydrogen carbonate (1·5 g.), and extracted with ether to give β-methylbutyrolactone (0·75 g.), b. p. 89°/14 mm., n_D^{20} 1·4327 (Found: C, 60·1; H, 8·2. Calc. for $C_5H_8O_2$: C, 60·0; H, 8·05%). The lactone (0·25 g.) was oxidised by heating it with sodium dichromate (1·3 g.) in 50% aqueous sulphuric acid (2·5 c.c.) and water (7·5 c.c.) for 4 hours at 100°. Extraction with ether gave methylsuccinic acid (0·13 g.), which crystallised from ethyl acetate–light petroleum in prisms, m. p. and mixed m. p. 112—113°.

(*b*) The acid (0·2 g.) in water (10 c.c.) was hydrogenated in the presence of a 20% palladium-on-charcoal catalyst (0·05 g.); 1·8 mols. of hydrogen were absorbed in 2 hours. Distillation of the filtered solution under reduced pressure gave only a small acidic residue (0·04 g.), but the distillate had a strong odour of *iso*valeric acid and required 11·5 c.c. of 0·1N-sodium hydroxide for neutralisation to phenolphthalein. Evaporation of this solution gave a sodium salt, which was identified by conversion into *p*-phenylphenacyl *iso*valerate, m. p. and mixed m. p. 79°.

Hydrogenation of γ-Hydroxycrotonic Acid.—The acid (0·2 g.), kindly supplied by Dr. P. Bladon, was hydrogenated in water (10 c.c.) over a 20% palladium-on-charcoal catalyst (0·05 g.) and absorbed

1·5 mols. of hydrogen in 1·5 hours. The solution was filtered and distilled. The distillate had a pronounced odour of butyric acid and required 7·5 c.c. of 0·1N-sodium hydroxide for neutralisation. It gave *p*-phenylphenacyl butyrate, m. p. 83·5—84°, undepressed on admixture with an authentic specimen. Drake and Bronitsky (*J. Amer. Chem. Soc.*, 1930, **52**, 3715) and Kögl and Sparenburg (*Rec. Trav. chim.*, 1940, **59**, 1180) give m. p. 97°, whereas Kircher, Prater, and Haagen-Smit (*Ind. Eng. Chem., Anal.*, 1946, **18**, 31) give m. p. 82°.

Proof of Structure of α-Hydroxy-β-methylenebutyric Acid.—Ozonisation. The acid (0·5 g.) in acetic acid (10 c.c.) was ozonised for 1 hour. The wash-water gave the dimedon derivative, m. p. 188°, of formaldehyde and a further quantity was obtained after steam-distillation of the acetic acid solution in the presence of zinc dust. This distillate also gave the 2 : 4-dinitrophenylosazone, m. p. 306°, of acetol on heating with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate.

Hydrogenation. The acid (0·4 g.), containing traces of γ-hydroxy-β-methylcrotonic acid, was hydrogenated in water (10 c.c.) in the presence of a 20% palladium-on-charcoal catalyst for 7½ hours, whereafter absorption of hydrogen (1·07 mols.) ceased. The filtered solution was evaporated to remove water and *iso*valeric acid, and gave a solid residue of α-hydroxy*iso*valeric acid, which crystallised from light petroleum in prisms (0·24 g.), m. p. and mixed m. p. 83—85°. The authentic material was prepared by treatment of α-bromo*iso*valeric acid with excess of 3N-aqueous sodium hydroxide at *ca.* 20° for 24 hours. The p-*phenylphenacyl* ester crystallised from alcohol in flattened needles, m. p. 108° (Found : C, 73·2; H, 6·15. $C_{19}H_{20}O_4$ requires C, 73·05; H, 6·45%). No hydrogen was absorbed when α-hydroxy*iso*valeric acid (0·2 g.) was treated as above in aqueous solution (10 c.c.) with the palladium catalyst (0·05 g.) for 6 hours; the unchanged acid was recovered.

Action of Aqueous Alkali on α-Hydroxy-β-methylenebutyric Acid.—The acid (0·02 g.), which gave a negative test with 2 : 4-dinitrophenylhydrazine sulphate, was dissolved in 5N-aqueous sodium hydroxide (5 c.c.) and heated for 45 minutes at 100°. The cooled solution was acidified with sulphuric acid and shown to contain α-keto*iso*valeric acid by formation of the 2 : 4-dinitrophenylhydrazone, m. p. 194°.

Reactivity of α-Chloro-αβ-unsaturated Acids with Alkoxides.—(*a*) *trans*-α-Chlorocrotonic acid (0·12 g.) in ethanol (0·8 c.c.) was treated with 2·6N-ethanolic sodium ethoxide (1·2 c.c.). The heterogeneous mixture was heated under reflux for 8 hours, then diluted with water, acidified with sulphuric acid, and extracted with ether. The halide in the aqueous portion was determined volumetrically, and corresponded to 36% reaction.

(*b*) α-Chloro-ββ-dimethylacrylic acid (0·135 g.) in ethanol (0·8 c.c.) and 2·6N-ethanolic sodium ethoxide (1·2 c.c.) (homogeneous solution) on similar treatment gave chloride ion equivalent to 86% reaction.

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